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On the Non-equilibrium Thermodynamics

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In the standard textbooks[1,2] of non-equilibrium thermodynamics, time-evolution of local thermodynamic variables is derived on the basis of conservation laws and local equilibrium assumption. The local entropy change is given in terms of entropy flow and local entropy production $\sigma[S]$. The local entropy production turns out to be sum of several terms, each of which is regarded as a product of two quantities; flux and conjugate force. For example, in the case of a multi-component fluid, which moves with velocity u , the local entropy production $\sigma[S]$ is given in the following form[1,2],

$$\sigma[S] = Q_k \frac{\partial}{\partial x_k} (1/T) + \sigma'_{ik} / T \cdot \frac{\partial u_i}{\partial x_k} - \sum_{\alpha=1}^n \rho_{\alpha} \Delta_{\alpha k} \left[\frac{\partial}{\partial x_k} (\mu_{\alpha}/T) - F_{\alpha k}/T \right] + \sum_r \frac{\partial \xi_r}{\partial t} A_r, \quad (1)$$

where i, k stand for spatial components, x, y, z , and we use summation convention. T is local temperature, $\vec{Q}(Q_k)$ is a vector representing heat flux. σ'_{ik} is stress tensor due to viscosity of the fluid. $\vec{\Delta}_{\alpha}(\Delta_{\alpha k})$ is the relative velocity of chemical component α with respect to convection velocity u . μ_{α} is chemical potential of the chemical component α . $\vec{F}_{\alpha}(F_{\alpha k})$ is an external force on unit mass of the chemical component α . ξ_r and A_r are extent and affinity of a chemical reaction r . Each term on the right hand side of Eq.(1) is interpreted as a product of flux and force; $\partial/\partial x_k (1/T)$ is force conjugate to heat flux Q_k , $-\partial u_i / \partial x_k / T$ is force conjugate to momentum flux (viscosity stress) σ'_{ik} , $-\partial/\partial x_k (\mu_{\alpha}/T) + F_{\alpha k}/T$ is force conjugate to diffusion flux $\rho_{\alpha} \Delta_{\alpha k}$ of the chemical component α , and, A_r/T is force conjugate to velocity of extent of the chemical reaction r .

However, it seems that the division of each term in the expression of the local entropy production into flux and force is not so definite. It is desired to have some general principle for determining fluxes and forces independently so that there would be no ambiguity in the division of each term in $\sigma[S]$ into flux and force. This problem was noted by Aono[3] some time ago.

The conventional local equilibrium assumption is the following; we assume, for change of local thermodynamic variables per unit mass, the same relations as those for a macroscopic equilibrium system, namely

$$Tds = de + pdv + \sum_{\alpha=1}^n \mu_{\alpha} dc_{\alpha} \quad (1)$$

where T is temperature, p is pressure, s , e , and v are entropy, internal energy and volume per unit mass. μ_{α} and c_{α} are chemical potential and mass concentration of chemical component α . When we deal with a fluid, which performs convective motion, it is better to take total energy (kinetic energy + potential energy + internal energy) and momentum as thermodynamic variables instead of simply taking internal energy as a variable describing states of the fluid, because they are conserved quantities. Hence, by noting that local total energy per unit mass ϵ is given by

$$\epsilon = u^2/2 + \Omega + e, \quad (2)$$

where Ω is local potential energy per unit mass, the relation (1) is extended to

$$Tds = d\epsilon - u_i du_i + p dv + \sum_{\alpha=1}^n (\mu_{\alpha} + \omega_{\alpha}) dc_{\alpha}. \quad (3)$$

Here we have introduced local potential energy per unit mass of the chemical component α ,

$$d\Omega = \sum_{\alpha=1}^n \omega_{\alpha} dc_{\alpha}, \quad -\partial \omega_{\alpha} / \partial x_k = F_{\alpha k}.$$

If we write the local equilibrium assumption (3) in terms of local densities of those thermodynamic quantities, we obtain

$$d(\rho s) = d(\rho \epsilon) / T - u_i d(\rho u_i) / T + \sum_{\alpha=1}^n (\mu_{\alpha} + \omega_{\alpha}) d\rho_{\alpha} / T, \quad (4)$$

where $\rho = \sum_{\alpha=1}^n \rho_{\alpha}$ is mass density of the fluid; $\rho = v^{-1}$. It is noted that the Gibbs-Duhem relation should also be extended to

$$\epsilon + p v - u^2 / 2 - T s - \sum_{\alpha=1}^n \omega_{\alpha} c_{\alpha} = \sum_{\alpha=1}^n \mu_{\alpha} c_{\alpha}, \quad (5)$$

along with (3). In other words, the chemical potential μ_{α} is different from the chemical potential in the absence of convection $\bar{\mu}_{\alpha}$ by $\mu_{\alpha} = \bar{\mu}_{\alpha} - u^2 / 2$.

We may divide $d\rho_{\alpha}$ into two parts; $d\rho_{\alpha} = d\rho_{\alpha}^{(diff)} + d\rho_{\alpha}^{(chem)}$, where $d\rho_{\alpha}^{(diff)}$ stands for the change of the density due to diffusion and $d\rho_{\alpha}^{(chem)}$ due to chemical reactions. If the external force is gravity or electric field, we may put $\sum_{\alpha=1}^n \omega_{\alpha} d\rho_{\alpha}^{(chem)} = 0$. Hence, we may rewrite (4) into the following expression which includes chemical reactions,

$$d(\rho s) = d(\rho \epsilon) / T - u_i d(\rho u_i) / T + \sum_{\alpha=1}^n (\mu_{\alpha} + \omega_{\alpha}) d\rho_{\alpha}^{(diff)} / T + \sum_r A_r d\xi_r / T, \quad (6)$$

where affinity A_r is defined in terms of stoichiometric constants $v_{\alpha r}$ [4],

$$A_r = - \sum_{\alpha=1}^n \mu_{\alpha} v_{\alpha r}. \quad (7)$$

Let us recall how thermodynamic forces are defined for a macroscopic system. Suppose the state of an isolated system is described by extensive quantities, x_1, x_2, \dots, x_N and entropy of the system is a function of these quantities $S(x_1, x_2, \dots, x_N)$. The differential of the entropy is given in the following form,

$$dS = \sum_{i=1}^N X_i dx_i \quad (8)$$

and we may call X_i "force". Indeed, if X_i is positive and large, then a small increment dx_i of the extensive quantity x_i gives rise to large increment of the entropy. In other words, according to the second law of thermodynamics, the positive large value of X_i may induce the increase of the extensive variable x_i in the system. The situation is more clearly illustrated when we consider two coupled systems A and B. Entropy and extensive quantities in each system are denoted by

superfixes A and B. Namely

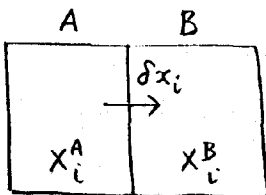
$$dS^A = \sum_{i=1}^N X_i^A dx_i^A, \quad dS^B = \sum_{i=1}^N X_i^B dx_i^B.$$

Suppose some amount δx_i of a physical quantity x_i is transported from A to B. Then the increase of total entropy is given by

$$\delta S = \delta S^A + \delta S^B = (X_i^B - X_i^A) \delta x_i.$$

Hence if $X_i^B > X_i^A$, this transport increases the total entropy.

In other words,



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$$\Pi_{ik}^R = \rho u_i u_k + p \delta_{ik}, \quad \Pi_{ik}^D = -\sigma'_{ik}. \quad (17)$$

The mass flux $\rho \vec{u}_\alpha$ is also divided into the reversible part \vec{J}_α^R and the dissipative part \vec{J}_α^D ; $\vec{J}_\alpha^R = \rho \vec{u}_\alpha$ (convection flux), $\vec{J}_\alpha^D = \rho \vec{\Delta}_\alpha$ (diffusion flux). (18)

The division of fluxes into reversible parts and dissipative parts seems reasonable since the reversible parts are, as is clear from their expressions, simply due to convection.

Up to now the argument is rather formal and there is no advantage in choosing, for the expression of entropy production, either (1) or (15). When we deal with linear thermodynamics, namely, when we relate the fluxes and forces by linear relations, it becomes rather serious how one defines forces and fluxes. Conventionally, the linear relations between fluxes and forces are given as

$$\begin{aligned} Q_k &= L_{kj} \frac{\partial}{\partial x_j} (1/T) - \sum_{\alpha=1}^n L_{k,\alpha j} \left[\frac{\partial}{\partial x_j} (\mu_\alpha/T) - F_{\alpha j}/T \right], \quad \sigma'_{ik} = L_{ik,mn} \frac{\partial u_n}{\partial x_m} / T \\ \rho_\alpha \Delta_\alpha &= L_{\alpha k, j} \left[\frac{\partial}{\partial x_j} (1/T) \right] - \sum_{\beta=1}^n L_{\alpha k, \beta j} \left[\frac{\partial}{\partial x_j} (\mu_\beta/T) - F_{\beta j}/T \right], \end{aligned} \quad (19)$$

where we have used Curie's principle. On the other hand, in our formulation, the linear relations between fluxes and forces should read, according to Curie's principle, as

$$\begin{aligned} Q_k - u_i \sigma'_{ik} + \sum_{\alpha=1}^n \rho_\alpha \omega_\alpha \Delta_\alpha &= L_{kj} \frac{\partial}{\partial x_j} (1/T) + \sum_{\alpha=1}^n L_{k,\alpha j} \left[- \frac{\partial}{\partial x_j} \left(\frac{\mu_\alpha + \omega_\alpha}{T} \right) \right], \quad \sigma'_{ik} = L_{ik,mn} \frac{\partial u_n}{\partial x_m} / T, \\ \rho_\alpha \Delta_\alpha &= L_{\alpha k, j} \left[\frac{\partial}{\partial x_j} (1/T) \right] - \sum_{\beta=1}^n L_{\alpha k, \beta j} \left[- \frac{\partial}{\partial x_j} \left(\frac{\mu_\beta + \omega_\beta}{T} \right) \right]. \end{aligned} \quad (20)$$

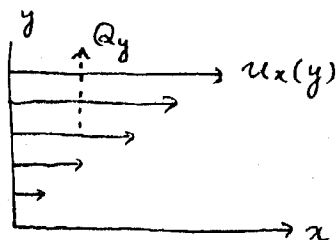
Let us consider, as an illustration, the following situation: There is only one chemical component; $\Delta=0$. There is no external force; $\omega_\alpha=0$ and $F_\alpha=0$. There is no temperature gradient and no chemical potential gradient. In this situation, the conventional linear relations give $\vec{Q}=0$ and $\sigma'_{ik} = L_{ik,mn} \partial u_n / \partial x_m / T$, the latter of which may be written in terms of viscosities,

$$\sigma'_{ik} = \eta \left(\frac{\partial u_i}{\partial x_k} + \frac{\partial u_k}{\partial x_i} \right) - \frac{2}{3} \delta_{ik} \text{div} \vec{u} + \zeta \delta_{ik} \text{div} \vec{u}. \quad (21)$$

On the other hand, our formulation leads to the following relations,

$$Q_k - u_i \sigma'_{ik} = 0 \quad \text{and} \quad \sigma'_{ik} = L_{ik,mn} \partial u_n / \partial x_m / T, \quad (22)$$

the latter of which can be written in terms of viscosities as given in Eq.(21). The first one implies that there still exists heat flow even in the absence of temperature gradient. As an illustration, let us consider a shear flow in



x-direction, $u_x(y)$ which is a function of the height y . Then, we have

$$\sigma'_{xy} = \sigma'_{yx} = \frac{\partial u_x}{\partial y}, \quad \sigma'_{ij} = 0 \text{ (otherwise).}$$

Hence we have heat flux in the y-direction,

$$Q_y = \frac{\eta}{2} \frac{\partial u_x}{\partial y}. \quad \text{Conventional linear thermodynamics}$$

tells $Q_y=0$.

After all, I have still a feeling of necessity of clarifying the concept and reality of "heat".

References: [1] L. Landau & E. Lifshitz, Fluid Mechanics; [2] P. Glansdorff & I. Prigogine, Structure, Stabilité et Fluctuations (Masson, 1971); [3] O. Aono, J. Stat. Phys. 5 113 (1972); [4] I. Prigogine & R. Defay, Chemical Thermodynamics (Longman 1954).

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the irreversible transport of x_i is caused by the difference of conjugate force X_i in neighboring cells because of the second law of thermodynamics. Hence it is reasonable to define thermodynamic forces for transport of conserved quantities by gradients of thermodynamic forces in the differential form of local entropy density, while the thermodynamic force for a chemical reaction is simply A_r/T (not gradient of A_r/T) because chemical reactions take place locally. Thus from Eq.(4), we may list up thermodynamic forces corresponding to thermodynamic quantities as Table 1.

Table 1 Thermodynamic Forces

Physical Quantities	Local Densities	Thermodynamic Forces
Total energy	$\rho\epsilon$	$\partial/\partial x_k (1/T)$
Momentum	ρu_i	$-\partial/\partial x_k (u_i/T)$
Diffusional mass	ρ_α (diff)	$-\partial/\partial x_k [(\mu_\alpha + \omega_\alpha)/T]$
Extent of chemical reaction	ξ_r	A_r/T

The time evolution of the local entropy density is derived from (4),

$$\frac{\partial(\rho s)}{\partial t} = \frac{1}{T} \frac{\partial(\rho\epsilon)}{\partial t} - \frac{u_i}{T} \frac{\partial(\rho u_i)}{\partial t} - \sum_{\alpha=1}^n \left(\frac{\mu_\alpha + \omega_\alpha}{T} \right) \frac{\partial(\rho_\alpha \text{diff})}{\partial t} + \sum_r \frac{A_r}{T} \frac{\partial \xi_r}{\partial t} \quad (9)$$

The time evolution of the local total energy density, the local momentum density, the local mass density is given from the conservation laws,

$$\frac{\partial(\rho\epsilon)}{\partial t} + \frac{\partial}{\partial x_k} \left[\rho u_k \left(\frac{u^2}{2} + \epsilon + \frac{P}{\rho} \right) + \sum_{\alpha=1}^n \rho_\alpha \omega_\alpha u_{\alpha k} + Q_k - u_i \sigma'_{ik} \right] = 0 \quad (\text{total energy conservation}) \quad (10)$$

$$\frac{\partial(\rho u_i)}{\partial t} + \frac{\partial}{\partial x_k} \Pi_{ik} = \rho F_i \quad (\text{momentum conservation}) \quad (11)$$

where $\Pi_{ik} = \rho u_i u_k + p \delta_{ik} - \sigma'_{ik}$, and $\rho \vec{F} = \sum_{\alpha=1}^n \rho_\alpha \vec{F}_\alpha$.

$$\frac{\partial}{\partial t} \rho_\alpha \text{diff} + \frac{\partial}{\partial x_k} \rho_\alpha u_{\alpha k} = 0 \quad (\text{mass conservation}). \quad (12)$$

From these conservation laws, we may derive the time evolution of the local entropy density in the following form,

$$\frac{\partial(\rho s)}{\partial t} + \text{div } \vec{S} = \sigma[S], \quad (13)$$

where the entropy flux \vec{S} is defined by

$$\vec{S} = \vec{Q}/T - \sum_{\alpha=1}^n \rho_\alpha \mu_\alpha \vec{\Delta}_\alpha / T + \rho s \vec{u} \quad \text{and} \quad \vec{\Delta}_\alpha = \vec{u}_\alpha - \vec{u}. \quad (14)$$

The local entropy production $\sigma[S]$ is the same expression as (1) but μ_α is now defined by (5). It is noted, however, that the expression of the entropy production (1) is not in terms of thermodynamic forces, just listed above. On the other hand, Eq.(1) can be alternatively written as

$$\sigma[S] = \left[Q_k - u_i \sigma'_{ik} + \sum_{\alpha=1}^n \rho_\alpha \omega_\alpha \Delta_{\alpha k} \right] \frac{\partial}{\partial x_k} (1/T) + (-\sigma'_{jk}) \left[-\frac{\partial}{\partial x_k} \left(\frac{u_i}{T} \right) \right] - \sum_{\alpha=1}^n \rho_\alpha \Delta_{\alpha k} \frac{\partial}{\partial x_k} \left(\frac{\mu_\alpha + \omega_\alpha}{T} \right) + \sum_r \frac{A_r}{T} \frac{\partial \xi_r}{\partial t} \quad (15)$$

Therefore we may define these factors multiplied on the thermodynamic forces as "fluxes"; in fact, these are "irreversible parts" of fluxes in the conservation laws. Thus the total energy flux \vec{J}_ϵ is divided into the reversible part \vec{J}_ϵ^R and the dissipative part \vec{J}_ϵ^D ;

$$(\vec{J}_\epsilon^R)_k = \rho u_k (\epsilon + P/\rho), \quad (\vec{J}_\epsilon^D)_k = \sum_{\alpha=1}^n \rho_\alpha \omega_\alpha \Delta_{\alpha k} + Q_k - u_i \sigma'_{ik}. \quad (16)$$

The momentum flux Π_{ik} can be also divided into the reversible part Π_{ik}^R and the dissipative part Π_{ik}^D ;